

## REPORT DOCUMENTATION PAGE

0333

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

|  |  |                         |  |  |  |
|--|--|-------------------------|--|--|--|
| 1. REPORT DATE (DD-MM-YYYY)<br>31-05-2004  |  | 2. REPORT TYPE<br>Final |  | 3. DATES COVERED (From - To)             |  |
| 4. TITLE AND SUBTITLE<br><br>Synthesis and Study of fullerene-based Photovoltaic and Two-photon Absorptive Conjugate Materials   |  |                         |  | 5a. CONTRACT NUMBER                      |  |
|  |  |                         |  | 5b. GRANT NUMBER<br>F49620-03-1-0334     |  |
|  |  |                         |  | 5c. PROGRAM ELEMENT NUMBER               |  |
|  |  |                         |  | 5d. PROJECT NUMBER                       |  |
| 6. AUTHOR(S)<br><br>Long Y. Chiang   |  |                         |  | 5e. TASK NUMBER                          |  |
|  |  |                         |  | 5f. WORK UNIT NUMBER                     |  |
|  |  |                         |  | 8. PERFORMING ORGANIZATION REPORT NUMBER |  |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)<br><br>Department of Chemistry, Institute of Nanoscience and Engineering Technology, University of Massachusetts Lowell, Lowell, MA 01854 |  |                         |  |  |  |
| 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  |  |                         |  | 20040706 006                             |  |

## 12. DISTRIBUTION / AVAILABILITY STATEMENT

Approve for Public Release: Distribution Unlimited.

## 13. SUPPLEMENTARY NOTES

## 14. ABSTRACT

We have achieved in the synthesis of several modified fluorenylated monoadducts of  $C_{60}$  showing high cross-sections of two-photon absorption (TPA). Conclusively, we substantiated our proposal that multi-adduct chromophore structures in close vicinity of the  $C_{60}$  cage may mimicking the extra-dimensionality of chromophores in 3D configuration, and thus contribute to the enhanced two-photon absorption optical properties. Accordingly for this study, several monoadducts and novel multiadduct analogues of  $C_{60}$ -diphenylaminofluorene  $C_{60}(>>DPAF)_n$  derivatives were synthesized and characterized by various spectroscopic methods.

In summary, effective molecular TPA cross-sections of one branched alkyl derivative  $C_{60}(>>DPAF-C_9)$  in  $CS_2$  was found to be  $251 \times 10^{-48} \text{ cm}^4\text{-sec/molecule}$ , which is slightly higher than the TPA cross-sections value ( $196 \times 10^{-48} \text{ cm}^4\text{-sec/molecule}$ ) obtained for our first generation  $C_{60}(>>DPAF-C_2)$  monoadduct. It is more than double in the cross-sections of its parent linear DPAF analogue and in a comparable value with that of the current TPA benchmark octupolar analogue AF350 with  $\sigma_2' = 278 \times 10^{-48} \text{ cm}^4\text{-sec/molecule}$ . As the structure of  $C_{60}$ -diphenylaminofluorene conjugate is extended from monoadduct to bisadduct analogous, effective molecular TPA cross-sections of  $C_{60}(>>DPAF-C_9)_2$  was found to be  $622 \times 10^{-48} \text{ cm}^4\text{-sec/molecule}$ . *This cross-sections value becomes one of the highest obtained for many organic polyaromatic chromophores to date.*

## 15. SUBJECT TERMS

|                                 |             |              |                            |                     |   |
|---------------------------------|-------------|--------------|----------------------------|---------------------|---|
| 16. SECURITY CLASSIFICATION OF: |             |              | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON           |
| a. REPORT                       | b. ABSTRACT | c. THIS PAGE |                            |                     | 19b. TELEPHONE NUMBER (include area code) |

## Synthesis and Study of fullerene-based Photovoltaic and Two-photon Absorptive Conjugate Materials

Long Y. Chiang

*Department of Chemistry, Institute of Nanoscience and Engineering Technology,  
University of Massachusetts Lowell, Lowell, Massachusetts*

### SUMMARY OF REPORT

During the funded research period and extended period to early 2004, we have achieved in the synthesis of several modified fluorenylated monoadducts of  $C_{60}$  showing high cross-sections of two-photon absorption (TPA). Conclusively, we substantiated our proposal that multi-adduct chromophore structures in close vicinity of the  $C_{60}$  cage may mimicking the extra-dimensionality of chromophores in 3D configuration, and thus contribute to the enhanced two-photon absorption optical properties. Accordingly for this study, several monoadducts and novel multiadduct analogues of  $C_{60}$ -diphenylaminofluorene  $C_{60}(>>DPAF)_n$  derivatives were synthesized and characterized by various spectroscopic methods.

In summary of measured TPA properties of  $C_{60}$ -diphenylaminofluorene conjugates, effective molecular TPA cross-sections of one branched alkyl derivative  $C_{60}(>>DPAF-C_9)$  in  $CS_2$  under a linearly polarized 800 nm pulsed beam was found to be  $251 \times 10^{-48} \text{ cm}^4\text{-sec/molecule}$ , which is slightly higher than the TPA cross-sections value ( $196 \times 10^{-48} \text{ cm}^4\text{-sec/molecule}$ ) obtained for our first generation  $C_{60}(>>DPAF-C_2)$  monoadduct, reported previously. It is more than double in the cross-sections of its parent linear DPAF analogue. It is also in a comparable value with that of the current TPA benchmark for AFX series of chromophore, denoted as octupolar analogue AF350, which showed  $\sigma_2' = 278 \times 10^{-48} \text{ cm}^4\text{-sec/molecule}$  at 800 nm pumping in THF. As the structure of  $C_{60}$ -diphenylaminofluorene conjugate is extended from monoadduct to bisadduct analogous, effective molecular TPA cross-sections of  $C_{60}(>>DPAF-C_9)_2$  in  $CS_2$  under a linearly polarized 800 nm pulsed beam was found to be  $622 \times 10^{-48} \text{ cm}^4\text{-sec/molecule}$ . *This cross-sections value becomes one of the highest obtained for many organic polyaromatic chromophores to date. The effective molecular TPA cross-sections value increases significantly by a factor of nearly 2.5 from that of  $C_{60}(>>DPAF-C_9)$ .* We propose hypothetically that a certain degree of hyperconjugation between of the  $C_{60}$  cage and the extended  $\pi$ -orbital of keto-DPAF moieties may make effective large area coverage of TPA cross-sections.

Optical absorption of these samples indicated a systematic increase in relative intensity of the fluorene band centered at 415 nm as the number of DPAF addend increases. Fluorescence of diphenylaminofluorene chromophore in all  $C_{60}(>>DPAF)_n$  derivatives as  $n = 1$ ,  $n = 2$ ,  $n = 3$ , and  $n = 4$  in *o*-dichlorobenzene and chloroform was found to be efficiently quenched as the direct covalent bond attachment of diphenylaminofluorene moieties to the fullerene cage facilitates efficient intramolecular electron or energy transfer processes.

In regard to optical limiting measurements of diphenylaminofluorene monoadduct of fullerene  $C_{60}$ (>DPAF- $C_{18}$ ) using a laser source at 532 nm with a 10 ns pulse, we observed the occurrence clear non-linear optical absorption behavior at the on-set incident laser power intensity of 100 MW/cm<sup>2</sup>. The initial transmittance of the solution is roughly 55–60%. As the incident power intensity increases above 100 MW/cm<sup>2</sup>, the transmitted power intensity is not linearly proportional to the incident intensity. The deviation progressively lowered the transmittance to 30% at the incident power intensity of 1200 MW/cm<sup>2</sup> that allowed a transmitted power intensity of 400 MW/cm<sup>2</sup>.

## STATEMENT OF OBJECTIVES

This research project focuses mainly on (A) the design and synthesis of fullerene-based two-photon absorptive (TPA) conjugate materials for sensor and personnel protection applications with a minor effort on (B) the design and synthesis of starburst fullerene-linked conjugated oligomer for grafting on the surface of interconnected TiO<sub>2</sub> nanoparticles toward fabrication of photovoltaic cells and modules. In the event of sufficient funding provided, we will increase the research activity of photovoltaic study using  $C_{60}$  derivatives as acceptors in conjunction with TiO<sub>2</sub> materials.

In the first subject of objective, we design and synthesize fullerene-based two-photon absorptive conjugated unsymmetrical starburst and dendritic macromolecules aiming to increase the dimensionality of two-photon absorption chromophore moiety. The first phase of the approach involves synthesis of several monoadduct and bisadducts of  $C_{60}$ -diphenylamino-diethylfluorene ( $C_{60}$ -DPAF) conjugates. In the next phase of the project, we will extend the synthetic work into the preparation of more complex trisadducts and tetrakisadducts of  $C_{60}$ -diphenylaminodiethylfluorene conjugates. That makes the  $C_{60}$  cage as an effective dimensionality coordinator and linker of highly condensed and packed diphenylamino-diethylfluorene moiety in 3D. The compound consists of direct bonding of multiple TPA absorptive chromophores on a  $C_{60}$  cage resulting in a starburst structure. The synthesis requires modified fullerene chemistry to be developed for providing conjugative chemical bonding between fluorene subunits and the fullerene cage. Coupling of fullerene  $\pi$ -orbitals with electron-accepting (A) characteristics, and the  $\pi$ -electron-donating (D) diphenylamino-diethylfluorene moieties produces 3-D  $(D_1)_n$ -A- $(D_2)_m$  macromolecules.

Extension of the  $C_{60}$ -DPAF structure from linear to starburst should progressively enhance the solubility of resulting conjugates. If  $D_1$  is well-defined monoadduct ( $n = 1$ ), the total proton integration of  $D_2$  moieties over the proton integration ratio of the  $D_1$  moiety will allow us to determine the number of  $n$  and  $m$  in the isolated product of  $(D_1)_n$ -A- $(D_2)_m$  macromolecules, using <sup>1</sup>H NMR spectroscopic method.

Upon modification of  $D_1$  and  $D_2$  DPAF moieties to incorporate long alkyl chains and highly branched alkyl chains, the softening temperature of the resulting  $(D_1)_n$ -A- $(D_2)_m$

macromolecules may be lowered into a range of 60–80 °C for easy processing of coating. High enthalpy uptake at the thermal melting transition may be used to enhance the heat dispersion upon sharp heating-up of the film material by an external laser power source.

Utilization of symmetrical octahedral hexamethofullerene as a connecting center allows us to design a *single macromolecule* of starburst  $C_{60}$ -(DPAF)<sub>6</sub> or 12. The use of hexanitrofullerene as a precursor core for attaching 6 TPA-active arms should lead to *unsymmetrical* starburst macromolecules for inhibiting ordered packing of TPA moieties in the solid state. All these  $C_{60}$ -DPAF dyes are ideal for systematic study of structure-property relationship, the number density, spatial effect, and synergetic interactions, as a cooperative effect, of individual TPA-responsive subunits within the 3-D molecular systems.

Based on our recent study on the photoinduced transient spectroscopy of  $C_{60}$ -DPAF monoadduct, solvent-dependent behavior of both intramolecular electron-transfer and energy-transfer from photoexcited DPAF moiety to the  $C_{60}$  cage was observed. Application of these phenomena based on  $(D_1)_n$ -A- $(D_2)_m$  macromolecules may include photodynamic therapy, drug delivery, and electrooptical devices.

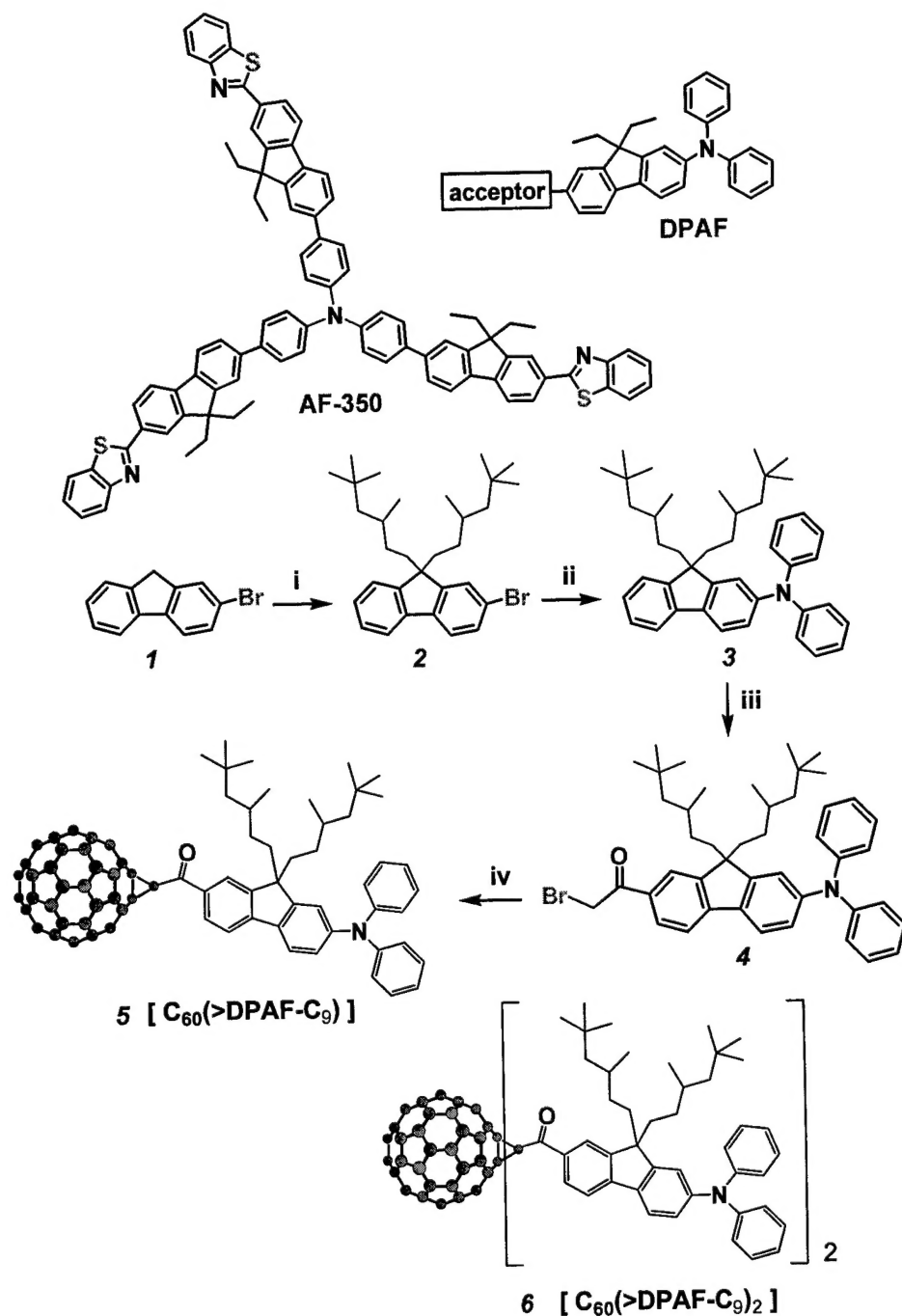
## RELATED MATERIALS APPLICATIONS

At least two types of optical physical properties of  $C_{60}$ -(DPAF)<sub>n</sub> conjugates were studied.

- (A) **Two-photon absorption properties** of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-(3,5,5-trimethylhexyl)-2-diphenylamino fluorene monoadduct [ $C_{60}$ (>DPAF- $C_9$ )] and bisadduct  $C_{60}$ (methanocarbonyl-9,9-(3,5,5-trimethylhexyl)-2-diphenylamino fluorene)<sub>2</sub> [ $C_{60}$ (>DPAF- $C_9$ )<sub>2</sub>].

As an effort to reduce the melting point of the two-photon absorbing material and minimize the dimerization or aggregation of the fullerene-DPAF conjugates, we modify the structure to used branched 3,5,5-trimethylhexyl groups for increasing the steric hindrance around the planar DPAF moiety.

As shown in the Scheme 1, the synthetic route included preparation of the key intermediate 7-bromoacetyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylamino fluorene **4** from 7-bromo-9,9-di(3,5,5-trimethylhexyl)-2-diphenylamino fluorene **3**. Synthesis of  $\alpha$ -bromoacetyl-diphenylamino fluorene **4** was found to be effective using direct Friedel-Crafts acylation of the compound **3** with  $\alpha$ -bromoacetyl bromide (1.2 equiv.) in presence of aluminum chloride (1.1 equiv.). This reaction was carried out in 1,2-dichloroethane at 0 °C to ambient temperature for a period of 4.0 h to afford the yellow crystalline product of **4** in a roughly 65% yield. Subsequent Bingel cyclopropanation reaction of  $\alpha$ -bromoacetyl fluorene derivative **4** with  $C_{60}$  in toluene in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.0 equiv.) at ambient temperature for 5 h led to formation of isomerically pure [6,6] closed fullerene monoadduct **5** of 7-(1,2-dihydro-



**Scheme 1.** Reagents and synthetic conditions: i, Et-I, NaOH, TBA-Br, toluene, 60 °C, 8 h; ii, diphenylamine, tris(dibenzylideneacetone)dipalladium(0) (cat), *rac*-BINAP (cat), *t*-BuONa, toluene, 110 °C, 8 h; iii, bromoacetyl bromide, AlCl<sub>3</sub>, ClCH<sub>2</sub>CH<sub>2</sub>Cl, 0 °C to r.t., 4 h; iv, C<sub>60</sub>, DBU, toluene, r.t., 5 h.

1,2-methanofullerene[60]-61-carbonyl)-9,9-di(3,5,5-trimethylhexyl)-2-diphenylamino fluorene [ $C_{60}(>>DPAF-C_9)$ ] as greenish brown solids in 70 % yield (based on recovered  $C_{60}$ ). This reaction also accompanied with the corresponding bisadduct **6** of  $C_{60}$ (methanocarbonyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylamino fluorene)<sub>2</sub> [ $C_{60}(>>DPAF-C_9)_2$ ] as brownish solids in a minor quantity of roughly 10%. Separation of **5** ( $R_f = 0.6$ ) and **6** ( $R_f = 0.3$ ) was carried out via thin-layer chromatography (TLC,  $SiO_2$ ) using a solvent mixture of hexane:toluene/3:2 as eluent.

**Table 1.** Measured TPA cross-section values by using a pulsed tunable dye laser working at 800 nm and ~8 ns laser pulses.\*

| Chromophore / solvent           | $\lambda_{max}/nm$ (linear absorption) | $\sigma_2 (\times 10^{-20} cm^4/GW-molecule)$ | $\sigma_2' (\times 10^{-48} cm^4-sec/molecule)$ |
|---------------------------------|--|---|---|
| AF350 / THF                     | 400                                    | 112   | 278   |
| $C_{60}(>>DPAF-C_9)$ / $CS_2$   | 410                                    | 102   | 251   |
| $C_{60}(>>DPAF-C_9)_2$ / $CS_2$ | 410                                    | 251   | 622   |
| $C_{60}(>>DPAF-C_9)$ / THF      |  | 41.1  | 102   |

\* Experimental uncertainty  $\pm 15\%$ . The measurements were made by Guang S. He, Qingdong Zheng, Changgui Lu, and Paras N. Prasad at Institute for Lasers, Photonics and Biophotonics, SUNY, Buffalo.

Effective TPA cross-section values of **5**, **6**, and AF-350 in a solution concentration of 0.02 M were obtained by measuring the nonlinear transmissivity of a given sample as a function of the intensity of the input laser beam. The beam was provided by a pulsed tunable dye laser working at ~800 nm wavelength, ~8 ns pulse duration, and 10 Hz repetition rate. An optical path-length of 1.0 cm was applied. As a result, molecular two-photon absorption cross-sections ( $\sigma_2$  in an unit of  $cm^4/GW-molecule$ ) were obtained from the nonlinear absorption coefficient  $\beta$  of the sample. As shown in Table 1, an effective molecular TPA cross-sections value of  $102 \times 10^{-48} cm^4-sec/molecule$  for  $C_{60}(>>DPAF-C_9)$  **5** in THF under a linearly polarized 800 nm pulsed beam was obtained. It correlated to a lower solubility of **5** in THF that gave some scatterings at a high concentration of 0.02 M. Possible aggregation of **5** in THF into nanoparticles can not be ruled out.

Interestingly, effective molecular TPA cross-sections ( $\sigma_2' = h\nu\sigma_2$ ) of  $C_{60}(>>DPAF-C_9)$  **5** in  $CS_2$  under a linearly polarized 800 nm pulsed beam was found to be  $251 \times 10^{-48} cm^4-sec/molecule$ , which is slightly higher than the TPA cross-sections value ( $196 \times 10^{-48} cm^4-sec/molecule$ ) obtained for our first generation  $C_{60}(>>DPAF-C_2)$  monoadduct, reported previously. It is more than double in the cross-sections of its parent linear DPAF analogue.



**Table 2.** Measured TPA cross-section values by using a pulsed tunable dye laser working at 775 nm and ~160 fs laser pulses.

| Chromophore/solvent                               | $\lambda_{\max}/\text{nm}$ (linear absorption) | $\sigma_2 (\times 10^{-20} \text{ cm}^4/\text{GW-molecule})$ | $\sigma_2' (\times 10^{-48} \text{ cm}^4\text{-sec/molecule})$ |
|---|--|--|--|
| AF350 / THF                                       | 400  | 0.600  | 1.49   |
| $\text{C}_{60}(>\text{DPAF-C}_9) / \text{CS}_2$   | 410  | 0.123  | 0.306  |
| $\text{C}_{60}(>\text{DPAF-C}_9)_2 / \text{CS}_2$ | 410  | 0.332  | 0.824  |

Under similar measurement conditions for the consistency in comparison of materials optical properties, a comparable data of **5** with those of several good TPA chromophores, such as the octupolar analogue AF350 showing  $\sigma_2' = 278 \times 10^{-48} \text{ cm}^4\text{-sec/molecule}$  at 800 nm pumping in THF, was made. As AF-350 being the current TPA benchmark for AFX series of chromophore, TPA characteristics of the linear A- $sp^3$ -D monoadduct of  $\text{C}_{60}$ -DPAF **5** in the nanosecond regime are apparently approaching one of the best candidates for the TPA based technology evaluation. Since the number density is a significant factor in enhancing the TPA cross-sections, the fullerene cage should serve well as a nucleus center of the fluorene dye in increasing the dimensionality. Furthermore, this result also suggests that  $\text{C}_{60}$  with multiple DPAF branches may lead to similar cooperative interactions reported for a three-armed oxadiazole-triarylamine system similar to AF-350.

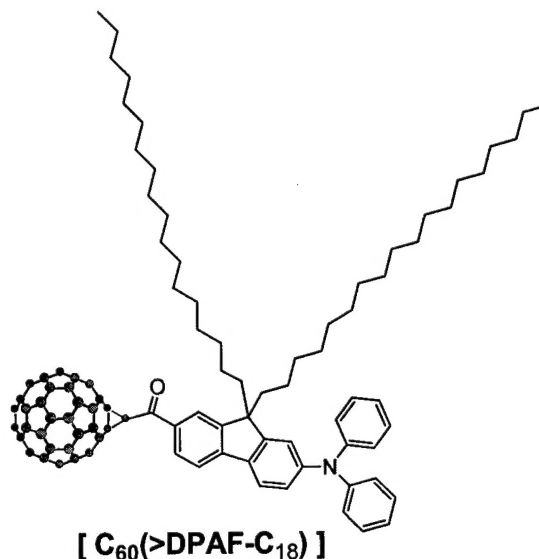
Accordingly, effective molecular TPA cross-sections of  $\text{C}_{60}(>\text{DPAF-C}_9)_2$  **6** in  $\text{CS}_2$  under a linearly polarized 800 nm pulsed beam was found to be  $622 \times 10^{-48} \text{ cm}^4\text{-sec/molecule}$ . *This cross-sections value becomes one of the highest obtained for many organic polyaromatic chromophores to date.* Apparently, by extending from the monoadduct analogous of fullerene to its bisadduct analogous, the effective molecular TPA cross-sections value increase significantly by a factor of nearly 2.5. We propose hypothetically that a certain degree of hyperconjugation between of the  $\text{C}_{60}$  cage and the extended  $\pi$ -orbital of two keto-DPAF moieties may make effective large area coverage of two-photon absorption cross-sections. The result substantiated our proposal that multi-adduct chromophore structures in close vicinity of the  $\text{C}_{60}$  cage may mimicking the extra-dimensionality of chromophores in 3D configuration, and thus contribute to the enhanced TPA optical properties.

**(B) Optical limiting properties** of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-dioctadecanyl-2-diphenylaminofluorene monoadduct [ $\text{C}_{60}(>\text{DPAF-C}_{18})$ ].

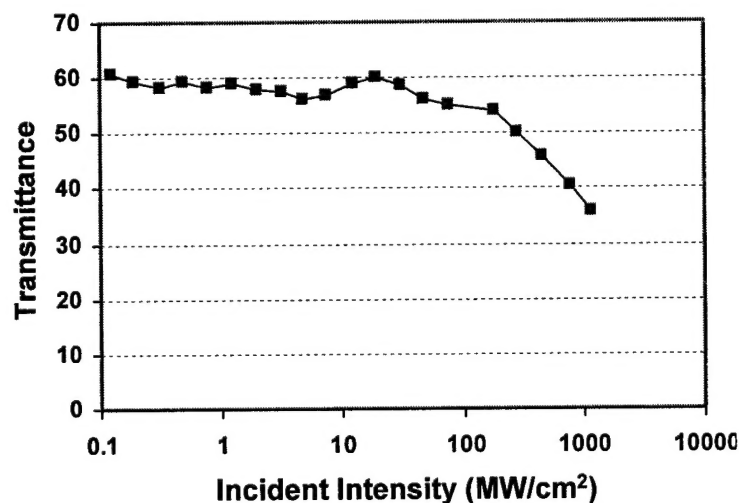
Optical limiting measurements of  $\text{C}_{60}$ -DPAF conjugates were made using a sample of diphenylaminofluorene monoadduct of fullerene  $\text{C}_{60}(>\text{DPAF-C}_{18})$  and a laser source at 532 nm with a 10 ns pulse. The experiments were performed in THF solution at incident laser power

intensity in the range of 0.1 to  $1.2 \times 10^3$  MW/cm<sup>2</sup> at U.S. Army Soldier, Biological, Chemical Command, Natick Soldier Center, Massachusetts.

The compound of C<sub>60</sub>(>DPAF-C<sub>18</sub>) was synthesized using a similar reaction sequence scheme shown in Scheme 1 involving Friedel-Crafts acylation of 7-bromo-9,9-dioctadecanyl-2-diphenylamino-fluorene with  $\alpha$ -bromoacetyl bromide in presence of aluminum chloride and Bingel cyclopropanation reaction of the resulting  $\alpha$ -bromoacetylfluorene derivative with C<sub>60</sub> in the presence of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU). Purification of C<sub>60</sub>(>DPAF-C<sub>18</sub>) was made by the chromatographic method (SiO<sub>2</sub>, toluene-THF).



As a result, we observed the occurrence clear non-linear optical absorption behavior at the on-set incident laser power intensity of 100 MW/cm<sup>2</sup>. The initial transmittance of the solution is roughly 55–60%. As the incident power intensity increases above 100 MW/cm<sup>2</sup>, the transmitted power intensity is not linearly proportional to the incident intensity. The deviation progressively

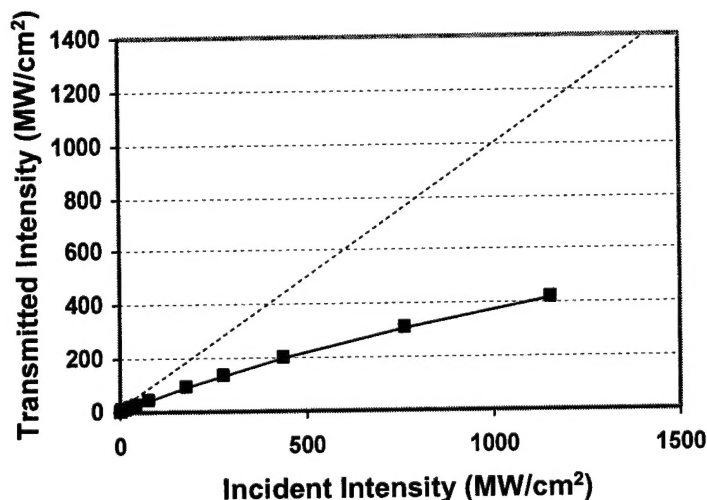


**Figure 1a.** Optical limiting characteristics of C<sub>60</sub>(>DPAF-C<sub>18</sub>) at the maximum incident laser power intensity of  $1.0 \times 10^3$  MW/cm<sup>2</sup>. Measurements were carried out by Dr. Brian Kimball, U.S. Army Soldier, Biological, Chemical Command, Natick Soldier Center, Massachusetts.

lowered the transmittance to 30% at the incident power intensity of 1200 MW/cm<sup>2</sup> that allowed a transmitted power intensity of 400 MW/cm<sup>2</sup>. Reproducible optical limiting behavior of at least two other samples of C<sub>60</sub>-diphenylamino-dialkylfluorene (C<sub>60</sub>-DPAF) conjugates was obtained very recently. These preliminary results indicated the possibility of formulating processible optical limiting polymer composites containing dispersion of C<sub>60</sub>-DPAF conjugates. The use of double long octadecanyl side chains on the diphenylamino-fluorene moiety decreases significantly solid characteristics of the material. Accordingly, semi-



solid paste of  $C_{60}(>>DPAF-C_{18})$  in the presence of a small portion of octadecane can be made at ambient temperature. Further study on the formulation of  $C_{60}(>>DPAF-C_{18})$  for producing the corresponding optical limiting liquid will be pursued.



**Figure 1b.** Optical limiting characteristics of  $C_{60}(>>DPAF-C_{18})$  at the maximum incident laser power intensity of  $1.2 \times 10^3 \text{ MW/cm}^2$ .

## INTRODUCTION OF SYNTHETIC DESIGN

Intermolecular and intramolecular electron transfer processes in functionalized fullerenes<sup>[1-6]</sup> were widely studied with the  $C_{60}$  cage as a potent electron acceptor in donor-acceptor assemblies, by taking advantage of its unique spherical shape for 3D attachments, electron delocalization capability, high chemical reactivity for functionalization, and rich electrochemical redox properties.<sup>[7-13]</sup> A variety of porphyrin analogue donor moieties in conjugation with  $C_{60}$ <sup>[14-18]</sup> forming the corresponding dyads were synthesized and widely explored for the study of photoinduced electron or energy transfer phenomena between donor and acceptor components, whereas the use of highly fluorescent diphenylaminofluorene (DPAF) in conjugation with  $C_{60}$  for the similar investigation was only recently reported<sup>[19, 20]</sup> by us. In addition, diphenylaminofluorene chromophore with large two-photon cross-sections can be utilized in photonic applications. High photostability of the fullerene cage may be advantageous in the photonic applications where a high intensity light source is used. Challenges are to increase the molecular two-photon cross-sections, without shifting the two-photon absorption peak away much from 800 nm, and the effective high TPA concentration in medium or density in solid state without inducing strong  $\pi$ - $\pi$  interaction stacking of chromophores.

Our study addresses the utilization of DPAF as a donor moiety acting as an antenna component for efficient light harvesting at visible wavelengths. That leads to the synthetic study

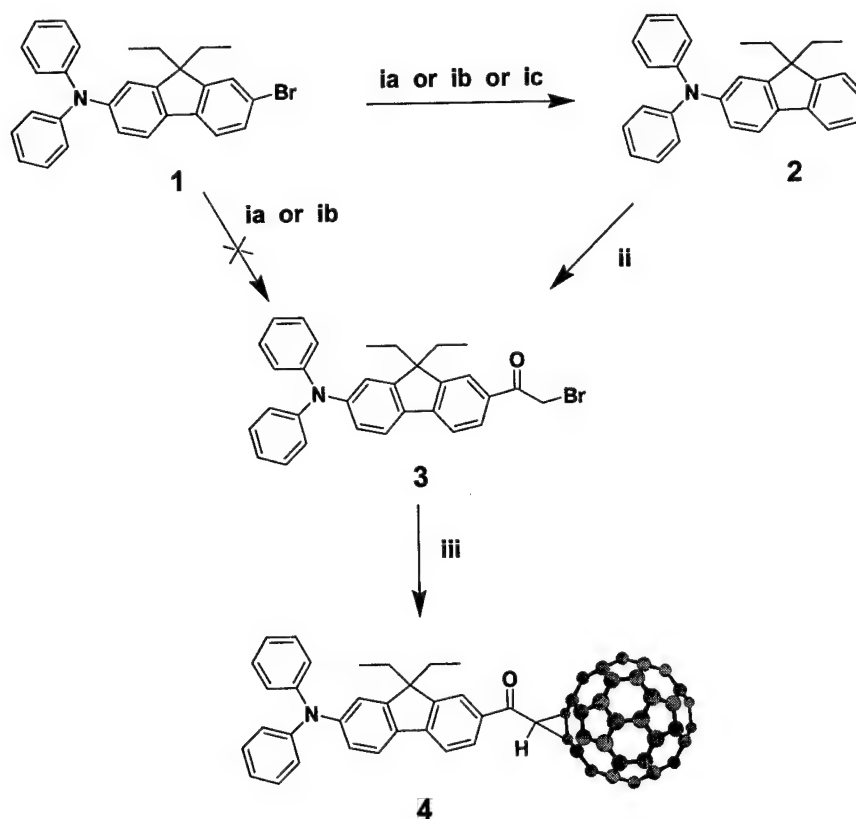
for preparation of several  $C_{60}$ -derived two-photon absorbing dendritic and starburst macromolecules to cooperatively enhancing the cross-sections value. Structure of these fullerene derivatives incorporates modified analogous of diphenylaminodiethylfluorene-based moieties. Combination of the  $C_{60}$  capability to exhibit reverse-saturable absorption in the visible region and the optical absorption of DPAF materials in the near-IR region may provide fundamental insights on the design of new and robust, broadband nanophotonic materials. Direct chemical bonding of multiple DPAF derivatives on a  $C_{60}$  cage forming a spherical star-like structure may enhance the overall cross-section of two-photon absorption and reduce the ability of TPA chromophores to aggregate orderly. The coupling of fullerenic  $\pi$ -orbitals with electron-accepting (A) characteristics and the  $\pi$ -electron-donating (D) diphenylaminodiethylfluorene moieties produces a 3-D system of  $(D)_n$ -A- $(D)_m$ .

Accordingly, we observed the first two-photon absorbing characteristics<sup>[19]</sup> of a  $C_{60}$ -DPAF conjugate linked by a keto functional group, in close resemblance to those reported for DPAF fluorophore-based 2D and 3D structures.<sup>[21-24]</sup> In addition, triarylamine derivatives usually bear a role of hole-transport mechanism in organic electroluminescent display devices.<sup>[25, 26]</sup> It is thus of our great interest to examine  $C_{60}$ -DPAF dyads in a donor-acceptor assembly using DPAF as a polarizable  $\pi$ -electron donor with inherent thermal and photochemical stability. This type of molecular assemblies may lead to potential applications in two-photon absorption based optoelectronics, organic light emitting diodes,<sup>[27]</sup> field-induced effect transistors,<sup>[28]</sup> and photovoltaic devices.<sup>[29, 30]</sup>

The first linear dyad, 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene as  $C_{60}( > \text{DPAF})$ , was found to be a highly two-photon absorbing chromophore with large cross-sections.<sup>[19]</sup> According to the hypothesis made in recent reports<sup>[22]</sup> on several DPAF related derivatives, enhancement of two-photon absorption cross-sections can be realized as their dimensionality is progressively increased. We investigate this analogy by the synthesis of several  $C_{60}( > \text{DPAF})_n$  conjugates with a systematic increase of the number of DPAF addends per  $C_{60}$  cage to postulate a simulation of the corresponding dimensional increase with the multiaddend attachment, followed by the measurement of their two-photon absorption cross-sections. Multidimensional  $C_{60}( > \text{DPAF})_n$  derivatives with enhanced two-photon absorption cross-sections may encompass important biological significance and lead to the development of technology related to photodynamic therapy, fluorescence bio-imaging, 3D optical data storage, and optical power limiting. In this article, we report the synthesis, material characterization, optical absorption, and fluorescence measurements of a linear  $C_{60}$ -DPAF dyad **4** and several fullerene derivatives **5**, **6** and **7** with multiple DPAF addends, showing effective quenching of the most of DPAF fluorescence.

## RESULTS AND DISCUSSION ON SYNTHETIC MATERIAL PREPARATION

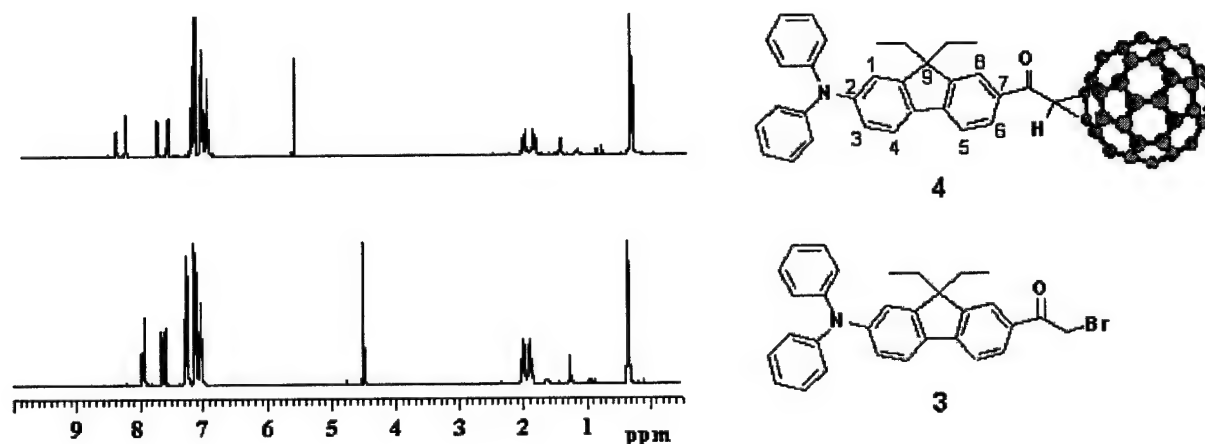
Synthetic procedure of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene monoadduct [4, C<sub>60</sub>(>DPAF)] is outlined in Scheme 2. Starting synthon 1 was conveniently synthesized by a reported procedure<sup>[21]</sup> starting from fluorene. It involved diethylation of fluorene at the C<sub>9</sub> carbon position using ethylbromide as a reagent to give 9,9-diethylfluorene. Subsequent monobromination of 9,9-diethylfluorene with *N*-bromosuccinimide afforded 2-bromo-9,9-diethylfluorene. Iodination of 2-bromo-9,9-diethylfluorene with iodic acid to 2-bromo-7-iodo-9,9-diethylfluorene was further converted to 7-bromo-9,9-diethyl-2-diphenylaminofluorene 1 via copper catalyzed amination reaction with diphenylamine.



**Scheme 2.** Reagents and the reaction condition, ia, Mg,  $\alpha$ -bromoacetyl bromide, THF; ib, *n*-butyllithium,  $\alpha$ -bromoacetyl bromide, THF; ic, *n*-butyllithium, THF, NH<sub>4</sub>Cl; ii, AlCl<sub>3</sub>,  $\alpha$ -bromoacetyl bromide, 1,2-dichloroethane; iii, C<sub>60</sub>, DBU, toluene.

The basis of the synthetic scheme to the product 4 relies on preparation of the key intermediate 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene 3 from 7-bromo-9,9-diethyl-2-diphenylaminofluorene 1. Effort to convert the compound 1 to 3 was made using bromide-

lithium metathesis with *n*-BuLi as a reagent at  $-78\text{ }^{\circ}\text{C}$  followed by treatment of the resulting 7-lithium-2-diphenylamino-9,9-diethylfluorene with  $\alpha$ -bromoacetyl bromide at low temperatures to replace the more reactive bromide atom. Alternatively, a Grignard complex was used instead of the lithium reagent. It was prepared from **1** with magnesium and subsequent treatment of the resulting Grignard intermediate with bromoacetyl bromide. In both cases, the reaction failed to give the expected product **3**, protonated 9,9-diethyl-2-diphenylaminofluorene **2** was formed instead. Apparently, the  $\alpha$ -proton of  $\alpha$ -bromoacetyl bromide is readily removed by either lithium or Grignard reagent. Structure of the product **2** was confirmed by its FAB mass spectrum showing the molecular ion at  $m/z$  389 and the corresponding fragmentation pattern. This spectrum is identical to that of **2** obtained by the quenching reaction of 7-lithium-2-diphenylamino-9,9-diethylfluorene intermediate with ammonium chloride. Synthesis of  $\alpha$ -bromoacetyldiphenylaminofluorene **3** was found to be effective using direct Friedel-Crafts acylation of the compound **2** with  $\alpha$ -bromoacetyl bromide (1.2 equiv.) in presence of aluminum chloride (1.1 equiv.). This reaction was carried out in 1,2-dichloroethane at  $0\text{ }^{\circ}\text{C}$  to ambient temperature for a period of 4.0 h to afford the yellow crystalline product of 7-bromoacetyl-9,9-



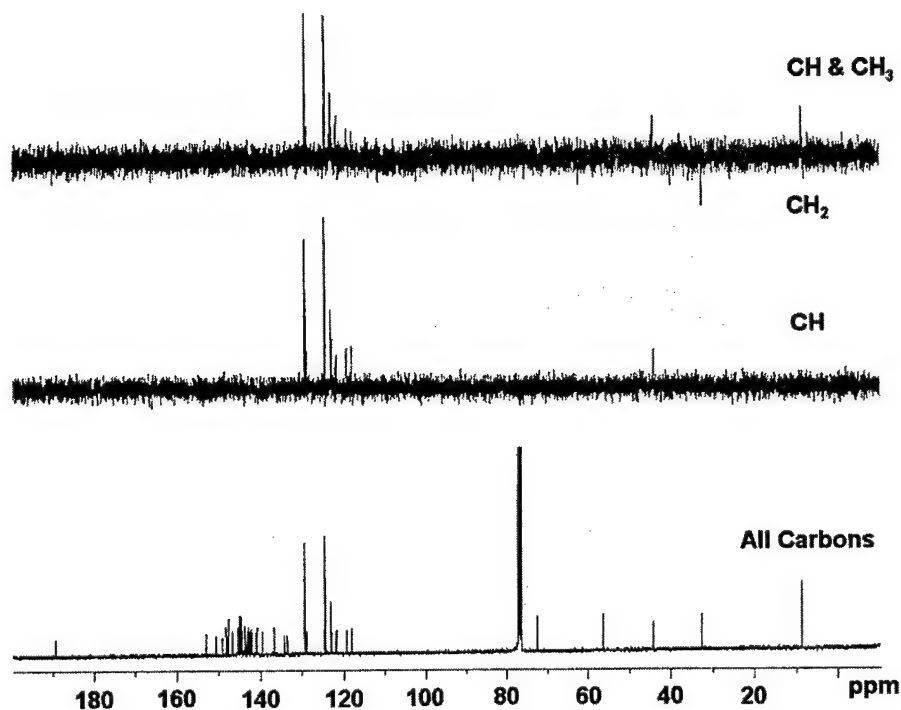
**Figure 2.**  $^1\text{H}$  NMR spectra of the starting  $\alpha$ -bromoacetyldiphenylaminofluorene derivative **3** and  $\text{C}_{60}$ (>DPAF) monoadduct **4** in  $\text{CDCl}_3$ .

diethyl-2-diphenylaminofluorene **3** in a roughly 66% yield.

Compound **3** showed a characteristic infrared band centered at  $1674\text{ cm}^{-1}$  in the FT-IR spectrum corresponding to the optical absorption of carbonyl stretching in **3** indicating attachment of  $\alpha$ -bromoacetyl group on the fluorene moiety. The molecular mass of **3** was confirmed by its positive ion mass spectrum (FAB $^+$ -MS) showing a group of molecular ion peaks with a maximum peak intensity at  $m/z$  509 and 511. Subsequent Bingel cyclopropanation<sup>[31]</sup> reaction of  $\alpha$ -bromoacetylfluorene derivative **3** with  $\text{C}_{60}$  in toluene in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.0 equiv.) at ambient temperature for 5 h led to

formation of isomerically pure [6,6] closed fullerene monoadduct **4** of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-diethyl-2-diphenylamino fluorene [ $C_{60}(>>DPAF)$ ] as greenish brown solids in 71 % yield (based on recovered  $C_{60}$ ). This reaction also accompanied with the corresponding bisadduct **5** of  $C_{60}(\text{methanocarbonyl-9,9-diethyl-2-diphenylamino fluorene})_2$  [ $C_{60}(>>DPAF)_2$ ] as brownish solids in a minor quantity of roughly 11%. Separation of **4** ( $R_f = 0.6$ ) and **5** ( $R_f = 0.3$ ) was carried out via thin-layer chromatography (TLC,  $SiO_2$ ) using a solvent mixture of hexane:toluene/3:2 as eluent.

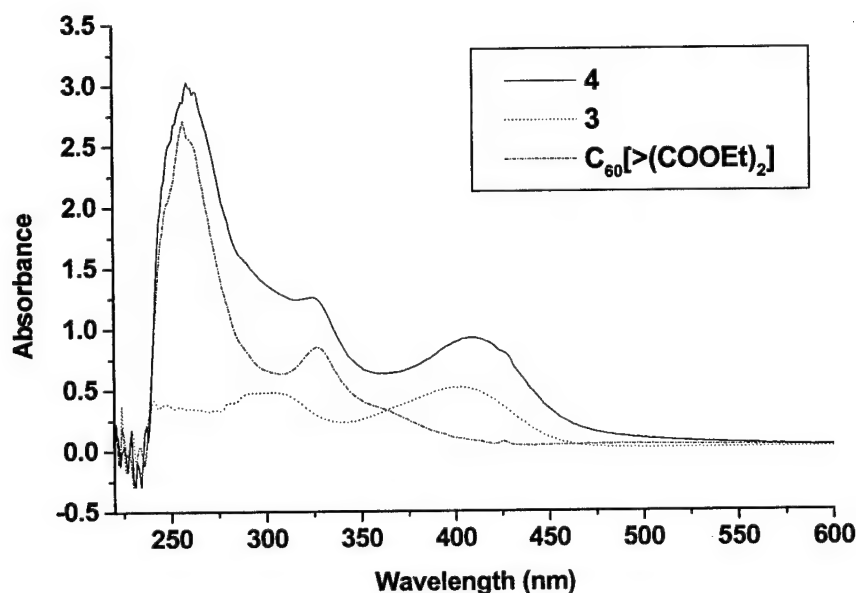
The compound  $C_{60}(>>DPAF)$  showed a strong absorption band of carbonyl stretching centered at  $1677\text{ cm}^{-1}$  with typical fullerene derivative signals at 750, 695 and  $534\text{ cm}^{-1}$  in FT-IR spectrum, consistent with the ketone formation that bridges fluorene and fullerene moieties. Observation of a group of mass peaks with a maximum peak intensity centered at  $m/z$  1149 in negative ion desorption chemical ionization mass spectrum (DCI-MS) of **4** clearly provides evidence of the molecular ion and composition of fullerene-fluorene dyad **4**.



**Figure 3.**  $^{13}C$ -DEPT NMR spectrum of methanofullerene-diphenylamino fluorene dyad  $C_{60}(>>DPAF)$  **4** in  $CDCl_3$ .

$^1H$  NMR spectra of **3** and **4** in  $CDCl_3$  exhibits the expected features with correct integration ratios as shown in Fig. 2. The corresponding spectrum of compound **3** shows one singlet proton peak at  $\delta$  4.49, corresponding to two methylene protons of  $\alpha$ -bromoacetyl group, and several

groups of aromatic proton peaks at  $\delta$  7.65 (d,  $J$  = 8 Hz), 7.95 (dd,  $J$  = 8 Hz,  $J$  = 1.6 Hz) and 7.92 (d,  $J$  = 1.4 Hz) corresponding to the chemical shift of the protons located at C<sub>5</sub>, C<sub>6</sub>, and C<sub>8</sub> atoms, respectively, of the fluorene moiety. Further reaction of **3** with C<sub>60</sub> to **4** caused a clear large downfield chemical shift of the  $\alpha$ -proton adjacent to the carbonyl group to  $\delta$  5.69, appearing as a singlet peak. It also accompanied with downfield chemical shifts of most of other fluorene protons at C<sub>5</sub>, C<sub>6</sub>, and C<sub>8</sub> to  $\delta$  7.83 (d,  $J$  = 8 Hz), 8.48 (dd,  $J$  = 8 Hz,  $J$  = 1.6 Hz), and 8.32 (d,  $J$  = 1.6 Hz), respectively, due to influence of the  $\pi$ -electronic structure of the fullerene cage. <sup>13</sup>C-DEPT NMR spectrum of **4** (Fig. 3) showed a characteristic carbonyl carbon peak appearing at  $\delta$  189.5 and terminal methyl and methylene carbon peaks at  $\delta$  8.6 and 32.5, respectively, corresponding to ethyl groups attached at C<sub>9</sub> consistent with the structure of **4**. All  $sp^2$  fullerene carbons appear as a total of 28 peaks in the region of  $\delta$  136 to  $\delta$  147 with two  $sp^3$  fullerene carbon peaks appearing at  $\delta$  72.6, indicating clearly a C<sub>2</sub> symmetry axis along the plane of two  $sp^3$  fullerene carbons. Those are <sup>13</sup>C NMR characteristics of typical methano[60]fullerene monoadducts confirming the overall structure of dyad **4**.



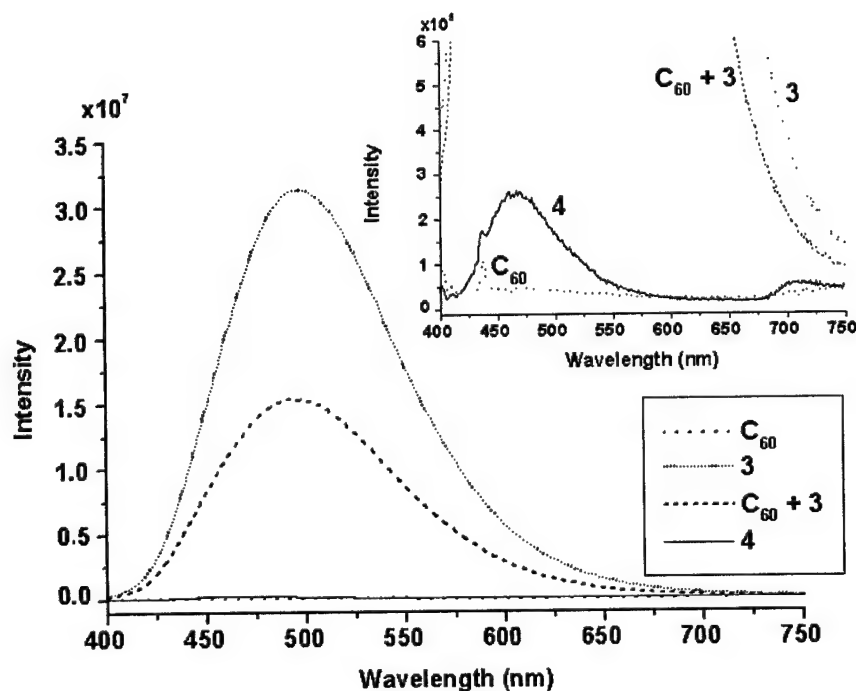
**Figure 4.** UV-Vis absorption spectra of the parent diphenylaminofluorene derivative **3**, C<sub>60</sub>(>DPAF) monoadduct **4**, and the fullerene core as C<sub>60</sub>[>(COOEt)<sub>2</sub>] in chloroform at a concentration of  $2.0 \times 10^{-5}$  M.

UV-Vis absorption spectrum (Fig. 4) of C<sub>60</sub>(>DPAF) dyad **4** showed three strong absorption bands centered at 259, 327 and 410 nm. Two of these bands centered at 259 and 327 nm are assigned to the optical absorption of the fullerene cage based on the comparison with that of methano[60]fullerene monomalonate diethylester C<sub>60</sub>[>(COOEt)<sub>2</sub>] while the third band centered at 410 nm is attributed to the DPAF moiety. The assignment reveals domination of the



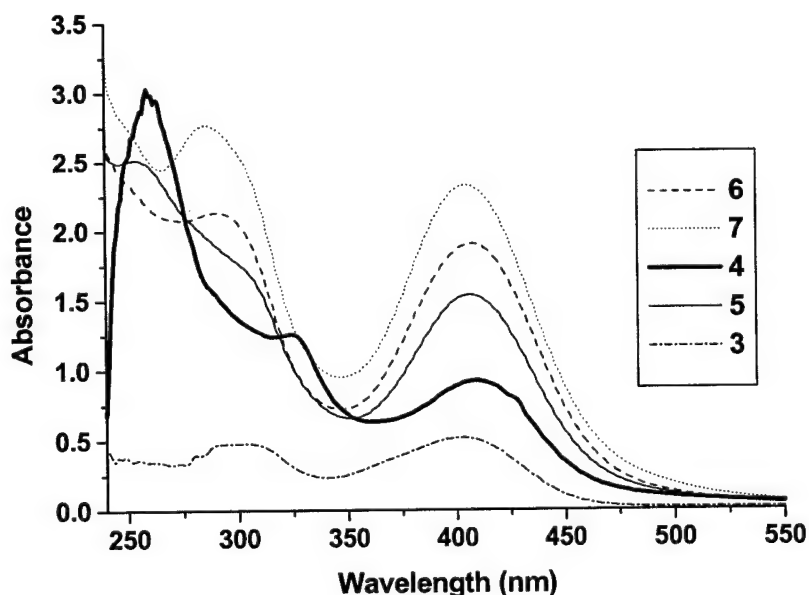
optical absorption of the fullerene cage in the UV region whereas the optical absorption of DPAF covers the visible region. Therefore, optical spectrum of the dyad **4** is a virtual superimposition of absorptions independently contributed from two chromophore moieties present in the molecule, indicating no appreciable ground state electronic interaction between two  $\pi$ -conjugated systems separated by a  $sp^3$  carbon.

In a solution of *o*-dichlorobenzene, DPAF **3** dye displays a strong fluorescence maximum centered at 497 nm (Fig. 5) upon photoexcitation at 385 nm. Under the same photoexcitation conditions and solution concentration, the emission spectrum of  $C_{60}$  and dyad **4** shows no and only an insignificant residual fluorescence, respectively, covering from 420 to 550 nm, as shown in the inset of Fig. 5. The observation indicated a nearly quantitative quenching of the DPAF fluorescence by the fullerene cage due to possible intramolecular electron or energy transfer processes. Efficiency of these processes decreases in the mixture of compound **3** and  $C_{60}$  in an equal molar quantity, as shown by the reduction in intensity of fluorescence maximum at 497 nm to 50% of the parent value without  $C_{60}$ . Intermolecular electron or energy transfer processes involve a biomolecular collision and are concentration dependent. Direct attachment of DPAF moieties onto one  $C_{60}$  cage increases the efficiency and kinetic rate of these transient processes. Interestingly, a weak fluorescence band of dyad **4** centered around 714 nm (inset of Fig. 5), which is the emission characteristic of methano[60]fullerene derivatives, was detected that may reveal the existence of neutral (uncharged) ground state of the fullerenic moiety.



**Figure 5.** Fluorescence emission profile of diphenylaminofluorene derivative **3**,  $C_{60}$ (>DPAF) monoadduct **4**,  $C_{60}$ , and ( $C_{60}$  + **3**) upon photoexcitation at 385 nm in *o*-dichlorobenzene at a concentration of  $2.0 \times 10^{-5}$  M.

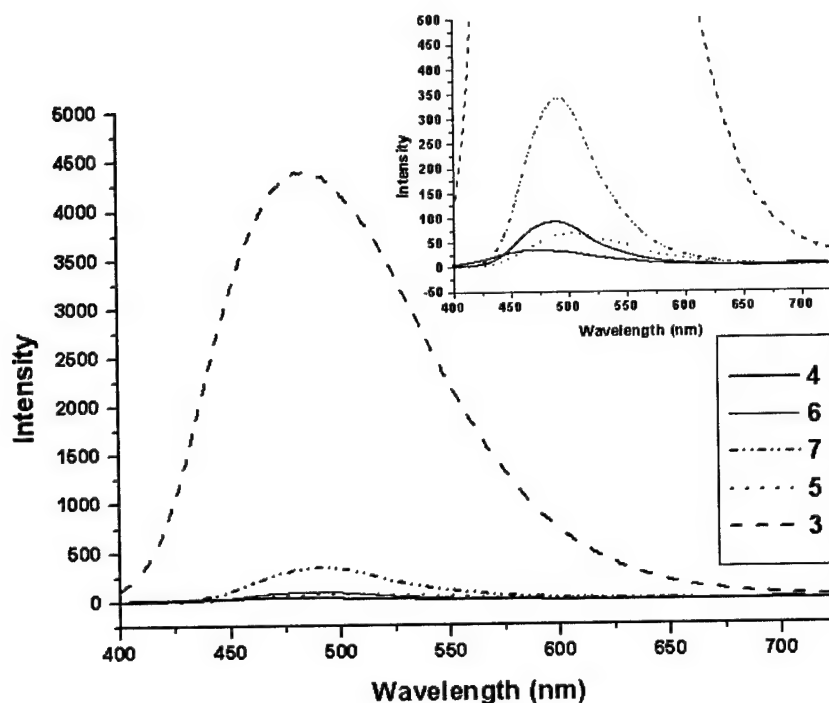
Characterization of the  $C_{60}(>>DPAF)_2$  bisadduct **5** was performed using the negative ion desorption chemical ionization mass spectroscopic study. The DCI-MS spectrum showed a group of mass peaks with a peak maximum at  $m/z$  1579 corresponding to the molecular ion mass of **5** consisting of two DPAF addends per  $C_{60}$  cage. Synthesis of  $C_{60}$ -DPAF conjugates containing a higher number of DPAF addends than 2 was performed by the treatment of  $C_{60}$  molecules with 8 equivalents of 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene **3** in presence of 1,8-diazabicyclo[5.4.0]undec-7-ene. Reaction progress was constantly monitored by taking samples for the TLC examination on sequential change of fullerene derivatives. Evidently, disappearance of  $C_{60}$  in the solution mixture was detected after 10 min of the reaction with systematic increase in intensity of two TLC spots corresponding to the monoadduct of  $C_{60}(>>DPAF)$  and the bisadduct of  $C_{60}(>>DPAF)_2$  derivatives with lower chromatographic polarity for the former. Intensity of these spots gradually decreased to an insignificant value after 6 h of the reaction. It accompanied with a number of new TLC spots in higher chromatographic polarity. The latter chromatographic profile remained almost constant even up to 36 h of the reaction. After a standard workup procedure, the crude products comprising of a mixture of  $C_{60}$ -DPAF conjugated derivatives were subjected to purification by repetitive preparative thin layer chromatographic (PTLC) separations until a narrow chromatographic band being isolated.



**Figure 6.** UV-Vis spectrum of **3**,  $C_{60}(>>DPAF)$  **4**,  $C_{60}(>>DPAF)_2$  **5**,  $C_{60}(>>DPAF)_3$  **6**, and  $C_{60}(>>DPAF)_4$  **7** in a concentration of  $2 \times 10^{-5}$  M in chloroform.

By using this separation technique, at least two major product bands were isolated for further characterization using negative ion desorption chemical ionization mass spectroscopic measurements. As a result, the DCI-MS spectrum of the product isolated from a narrow upper

band showed a group of mass peaks with a peak maximum at  $m/z$  2009 corresponding to the molecular ion mass of  $C_{60}(\text{methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene})_3$  **6** as  $C_{60}(>\text{DPAF})_3$ , consisting of three DPAF addends per  $C_{60}$  cage. The second narrow band led to a product showing a group of mass peaks with a peak maximum at  $m/z$  2437 corresponding to the molecular ion mass of  $C_{60}(\text{methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene})_4$  **7** as  $C_{60}(>\text{DPAF})_4$ , consisting of four DPAF addends per  $C_{60}$  cage. Several additional PTLC bands with higher chromatographic polarity were also isolated each in a small quantity. However, no conclusive DCI-MS data was obtained.



**Figure 7.** Fluorescence spectra of **3**,  $C_{60}(>\text{DPAF})$  **4**,  $C_{60}(>\text{DPAF})_2$  **5**,  $C_{60}(>\text{DPAF})_3$  **6**, and  $C_{60}(>\text{DPAF})_4$  **7** in chloroform upon photoexcitation at 385 nm under a concentration of  $2 \times 10^{-5}$  M.

$^1\text{H}$  NMR spectra of both trisadduct  $C_{60}(>\text{DPAF})_3$  and tetrakisadduct  $C_{60}(>\text{DPAF})_4$  showed broadening of all proton peaks with an increase in number of aliphatic and aromatic proton peaks. Especially, multiple peak characteristics of  $\alpha$ -proton adjacent to the carbonyl group of **6** and **7** may reveal a mixture of regioisomers in these products. Attempts are underway to separate a single regioisomer from **6** and **7** for the structural identification. UV-Vis spectra of bisadduct  $C_{60}(>\text{DPAF})_2$ , trisadduct  $C_{60}(>\text{DPAF})_3$ , and tetrakisadduct  $C_{60}(>\text{DPAF})_4$  are shown in Fig. 6, giving a similar optical absorption wavelength of DPAF moieties to that of monoadduct **4** centered at 410 nm. Evidently, as the number of DPAF addends per  $C_{60}$  cage increases in the corresponding derivatives going from monoadduct  $C_{60}(>\text{DPAF})$  to tetrakisadduct  $C_{60}(>\text{DPAF})_4$ ,

extinction coefficients of the visible absorption band at 410 nm increases systematically to a higher value while the sum of overall extinction coefficients of the UV bands corresponding to the optical absorption of fullerene moiety remaining relatively constant among **4**, **5**, **6**, and **7**. As the extinction coefficient of VU-Vis absorption bands is proportional to the concentration of absorbent moiety in the solution, a proportional increase in absorption intensity of the DPAF band may allow us to correlate the number of DPAF addends per C<sub>60</sub> cage among derivatives of **4**, **5**, **6**, and **7** and substantiate their composition. As shown in Fig. 7, fluorescence emission spectra of **3**, C<sub>60</sub>(>DPAF) **4**, C<sub>60</sub>(>DPAF)<sub>2</sub> **5**, C<sub>60</sub>(>DPAF)<sub>3</sub> **6**, and C<sub>60</sub>(>DPAF)<sub>4</sub> **7** all showed efficient fluorescence quenching of diphenylaminofluorene chromophore centered at 497 nm in chloroform upon photoexcitation at 385 nm.

## EXPERIMENTAL AND SYNTHETIC PROCEDURE

Fluorene was purchased from Aldrich Chemicals. All other chemicals were purchased from Acros Ltd. A C<sub>60</sub> sample in a purity of 99.5% was used. Further purification of C<sub>60</sub> was made by thin-layer chromatography (TLC, SiO<sub>2</sub>, toluene). Toluene and benzene were dried and distilled over sodium. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on either a Bruker Spectrospin-400 or Bruker AC-300 spectrometer. Mass spectroscopic studies were performed either by use of the positive ion fast atom bombardment (FAB<sup>+</sup>) technique with a direct probe on a JEOL SX-102A mass spectrometer or the negative ion desorption chemical ionization (DCI) technique with a direct probe on a JEOL JMS-SX 102A mass spectrometer. Infrared spectra were recorded as KBr pellets on a Nicolet 750 series FT-IR spectrometer. UV-Vis spectra were recorded on a Hitachi U-3410 UV spectrometer. Fluorescence spectra were recorded on a FLUOROLOG (ISA Instruments) spectrofluorometer.

### Synthesis of 9,9-diethyl-2-diphenylaminofluorene (**2**)

To a cooled solution (−78 °C) of 7-bromo-2-diphenylamino-9,9-diethylfluorene (1.0 g, 2.1 mmol) in dry THF (20 ml) under nitrogen atmospheric pressure was added *n*-BuLi in hexane (0.53 ml, 1.6 M, 8.5 mmol) over a period of 5 min. The reaction mixture was stirred for a period of 4 h while the bath temperature was raised slowly to −20 °C. It was quenched with saturated ammonium chloride solution (NH<sub>4</sub><sup>+</sup> Cl<sup>−</sup>). The products were extracted by chloroform (2 x 20 ml) and the combined organic extracts were washed with aqueous saturated ammonium chloride followed by water. The organic layer was dried over anhydrous sodium sulfate, concentrated in vacuo, and purified on thin-layer chromatographic plates (TLC, SiO<sub>2</sub>, R<sub>f</sub> = 0.9 using hexane:EtOAc in a ratio of 4:1 as eluent) to give 9,9-diethyl-2-diphenylaminofluorene **2** as viscous colorless oil in a yield of 95% (0.78 g). Spectroscopic data of **2**: FAB<sup>+</sup>–MS *m/z* 389 (M<sup>+</sup>); FT-IR (KBr)  $\nu_{\max}$  3058 (m), 3030 (m), 2956 (s), 2923 (s), 2868 (m), 1584 (vs), 1485 (vs), 1448 (s), 1326 (s), 1300 (s), 1268 (s), 751 (s), 733 (s), 698 (s), 694 (m), and 512 (m) cm<sup>−1</sup>; <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.64–7.57 (m, 2H), 7.33–7.23 (m, 7H), 7.15–7.12 (m, 5H), 7.06–6.99 (m, 3H), 1.99–1.87 (m, 4H), and 0.36 (t,  $J$  = 7.3 Hz, 6H).

### Synthesis of 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene (3)

A sample of 2-diphenylamino-9,9-diethylfluorene (1.0 g, 2.6 mmol) in 1,2-dichloroethane (15 ml) was added to the suspension of aluminum chloride (0.38 g, 2.8 mmol) in 1,2-dichloroethane (15 ml) at 0 °C. Bromoacetyl bromide (0.27 ml, 3.1 mmol) was added over a period of 10 min while maintaining the reaction temperature at 0–10 °C. The reaction mixture was allowed to reach ambient temperature gradually with stirring for 4 h. It was quenched by slow addition of water (50 ml). Organic layer was sequentially washed with dil. HCl (1N, 50 ml) and water (50 ml x 2). The solution was concentrated in vacuo, followed by purification via column chromatography (silica gel) using a solvent mixture of hexane:toluene/3:2 as eluent. After evaporation of the eluent solvent, a crude product of 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene **3** as yellow crystalline solids was obtained in a yield of 66% (0.87 g). Further purification was made on thin-layer chromatographic plates (TLC, SiO<sub>2</sub>,  $R_f$  = 0.3, using hexane:toluene/3:2 as eluent). Spectroscopic data of **3**: FAB<sup>+</sup>-MS  $m/z$  509, 511 ( $M^+$ ); UV-Vis (CHCl<sub>3</sub>,  $2.0 \times 10^{-5}$  M)  $\lambda_{\max}$  ( $\epsilon$ ) 251 ( $1.6 \times 10^4$ ), 290 ( $2.3 \times 10^4$ ), and 408 ( $2.7 \times 10^4$ ) nm; FT-IR (KBr)  $\nu_{\max}$  3037 (w), 2966 (s), 2928 (m), 2878 (w), 1674 (s), 1595 (vs), 1491 (s), 1281 (vs), 754 (s), and 698 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.95 (dd,  $J$  = 8 Hz,  $J$  = 1.6 Hz 1H), 7.92 (d, 1H), 7.65 (d,  $J$  = 8 Hz, 1H), 7.60 (d,  $J$  = 8 Hz, 1H), 7.28–7.09 (m, 10H), 7.05–7.02 (m, 2H), 4.49 (s, 2H), 2.05–1.84 (m, 4H), and 0.35 (t,  $J$  = 7.3 Hz, 6H).

### Synthesis of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene monoadduct [**4**, C<sub>60</sub>(>DPAF)] and bisadduct C<sub>60</sub>(methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene)<sub>2</sub> [**5**, C<sub>60</sub>(>DPAF)<sub>2</sub>]

C<sub>60</sub> (1.0 g, 1.4 mmol) and 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene (0.7 g, 1.4 mmol) were dissolved in toluene (700 ml) under an atmospheric pressure of nitrogen. To this was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.2 ml, 1.4 mmol) and stirred at room temperature for a period of 5 h. At the end of stirring, suspending solids of the reaction mixture were filtered off and the filtrate was concentrated to a 10% volume. Methanol (100 ml) was then added to cause precipitation of the crude product, which was isolated by centrifugation. The isolated solid was a mixture of monoadduct **4** and bisadduct **5**. Separation of **4** and **5** were made by column chromatography (silica gel) using a solvent mixture of hexane:toluene/3:2 as eluent. The first chromatographic band corresponding to  $R_f$  = 0.6 on the thin-layer chromatographic plate (TLC, SiO<sub>2</sub>, hexane:toluene/3:2) afforded 7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene **4** as greenish brown solid of C<sub>60</sub>(>DPAF) monoadduct in 71% yield (0.82 g, based on recovered C<sub>60</sub>). The second chromatographic band corresponding to  $R_f$  = 0.3 on the thin-layer chromatographic plate (TLC, SiO<sub>2</sub>,

hexane:toluene/3:2) gave the bisadduct **5**  $C_{60}(\text{methanocarbonyl-9,9-diethyl-2-diphenylamino-fluorene})_2$  [ $C_{60}(>>\text{DPAF})_2$ ] as brownish solids in a minor quantity of roughly 11% (0.17 g).

Spectroscopic data of **4**: negative ion desorption chemical ionization mass spectrum (DCI-MS)  $m/z$  1149 ( $M^+$ ); UV-Vis ( $\text{CHCl}_3$ ,  $2.0 \times 10^{-5}$  M)  $\lambda_{\text{max}}$  ( $\epsilon$ ) 256 ( $1.1 \times 10^5$ ), 327 ( $4.8 \times 10^4$ ), and 408 ( $3.5 \times 10^4$ ) nm; FT-IR (KBr)  $\nu_{\text{max}}$  3029 (w), 2963 (s), 2921 (m), 2875 (w), 2853 (w), 1677 (s), 1591 (vs), 1492 (s), 1276 (s), 750 (s), 695 (s), and 524 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  8.48 (dd,  $J = 8$  Hz,  $J = 1.6$  Hz, 1H), 8.32 (d,  $J = 1.6$  Hz, 1H), 7.83 (d,  $J = 8$  Hz, 1H), 7.66 (d,  $J = 8$  Hz, 1H), 7.29–7.11 (m, 10H), 7.07–7.03 (m, 2H), 5.69 (s, 1H), 2.13–1.89 (m, 4H), and 0.40 (t,  $J = 8$  Hz, 6H).

Spectroscopic data of **5**: FAB $^+$ -MS  $m/z$  1579 ( $M^+$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  8.7–8.2 (m, 4H), 7.9–7.7 (m, 2H), 7.7–7.5 (m, 2H), 7.4–7.2 (m, 20H), 7.2–7.0 (m, 4H), 5.6–5.3 (m, 2H), 2.1–1.9 (m, 8H), and 0.40 (m, broad, 12H).

**Synthesis of trisadduct  $C_{60}(\text{methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene})_3$  [**6**,  $C_{60}(>>\text{DPAF})_3$ ] and tetrakisadduct  $C_{60}(\text{methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene})_4$  [**7**,  $C_{60}(>>\text{DPAF})_4$ ]**

A solution of 7-bromoacetyl-9,9-diethyl-2-diphenylaminofluorene (0.14 g, 0.28 mmol, excess) in toluene was added to  $C_{60}$  (25 mg, 0.035 mmol) dissolved in dry toluene (25 ml) with stirring under nitrogen. To this solution was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 42 mg, 0.04 ml, 0.28 mmol) with continuous stirring. Reaction progress was monitored by taking samples on the TLC plate for following disappearance of the starting fluorine derivative and  $C_{60}$ . After a reaction period of 10 min, the absence of  $C_{60}$  on TLC was noticed. The reaction was allowed to continue with stirring for an additional 36 h with periodical TLC monitoring. At the end of reaction, the mixture was filtered, concentrated in vacuo to give a crude product mixture of **6**, **7** and possibly higher adducts. They were separated by different bands on preparative TLC plates ( $\text{SiO}_2$ ) using a mixture of chloroform and hexane as eluent. Further repurification and separation of each band by additional preparative TLC plates using a solvent mixture with decreasing polarity as eluent allowed a distinguishable narrow brown-yellow band of each sample to be isolated. Subsequent identification of these samples isolated from each purified band by their negative ion desorption chemical ionization mass spectrum (DCI-MS) clarified the molecular mass of a sample from one band corresponding to a regioisomeric mixture of  $C_{60}(\text{methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene})_3$  [**6**, a trisadduct  $C_{60}(>>\text{DPAF})_3$ ] in a yield of roughly 28 mg and the other molecular mass of a sample corresponding to a regioisomeric mixture of  $C_{60}(\text{methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene})_4$  [**7**, a tetrakisadduct  $C_{60}(>>\text{DPAF})_4$ ] in a yield of roughly 20 mg. The rest of minor bands on TLC plates were also isolated in an insignificant quantity of possibly higher fullerene-DPAF adducts.



Spectroscopic data of **6**: DCI<sup>+</sup>-MS *m/z* 2009 (M<sup>+</sup>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.6–8.0 (m, broad, 6H), 7.9–7.7 (m, broad, 3H), 7.7–7.4 (m, broad, 3H), 7.4–7.2 (m, broad, 30H), 7.2–6.9 (m, broad, 6H), 5.2–5.0 (m, 3H), 2.1–1.87 (m, broad, 12H), and 0.34 (t, broad, 18H). Spectroscopic data of **7**: DCI<sup>+</sup>-MS *m/z* 2437 (M<sup>+</sup>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.6–8.0 (m, broad, 8H), 7.9–7.7 (m, broad, 4H), 7.7–7.5 (m, broad, 4H), 7.3–7.2 (m, broad, 40H), 7.2–6.9 (m, broad, 8H), 5.2–5.0 (m, 4H), 2.1–1.8 (m, broad, 16H), and 0.34 (t, broad, 24H).

## REFERENCES

- Williams, R. M.; Koeberg, M.; Lawson, J. M.; An, Y.-Z.; Rubin, Y.; Paddon-Row, M. N.; Verhoeven, J. W. Photoinduced Electron Transfer to C<sub>60</sub> across Extended 3- and 11-Bond Hydrocarbon Bridges: Creation of a Long-Lived Charge-Separated State. *J. Org. Chem.* **1996**, *61*(15), 5055-5062.
- Canteenwala, T.; Anantharaj, V.; Patil, S. V.; Haldar, M.; Chiang, L. Y. Intramolecular Electron-Transfer of C<sub>60</sub>-oligoaniline Leucoemeraldine Conjugates upon photoactivation. *J. Macromol. Sci. – Pure Appl. Chem.* **2002**, *A39*, 1069-1083.
- Kuciauskas, D.; Liddell, P. A.; Moore, A. L.; Moore, T. A.; Gust, D. Magnetic Switching of Charge Separation Lifetimes in Artificial Photosynthetic Reaction Centers. *J. Am. Chem. Soc.* **1998**, *120*(42), 10880-10886.
- Guldi, D. M.; Gonzalez, S.; Martin, N.; Anton, A.; Garin, J.; Orduna, J. Efficient Charge Separation in C<sub>60</sub>-Based Dyads : Triazolino[4',5':1,2][60]fullerenes. *J. Org. Chem.* **2000**, *65*(7), 1978-1983.
- Segura, J. L.; Priego, E. M.; Martin, N.; Luo, C.; Guldi, D. M. A New Photoactive and Highly Soluble C<sub>60</sub>-TTF-C<sub>60</sub> Dimer: Charge Separation and Recombination. *Org. Lett.* **2000**, *2*(25), 4021-4024.
- Bracher, P. J.; Schuster, D. I. Electron transfer in functionalized fullerenes. *Developments in Fullerene Science.* **2002**, *4*, (Fullerenes: From Synthesis to Optoelectronic Properties), 163-212.
- Xie, Q.; Perez-Cordero, E.; Echegoyen, L. Electrochemical detection of C<sub>60</sub><sup>6-</sup> and C<sub>70</sub><sup>6-</sup> : Enhanced stability of fullerides in solution. *J. Am. Chem. Soc.* **1992**, *114*(10), 3978-3980.
- Zhou, F.; Jehoulet, C.; Bard, A. J. Reduction and electrochemistry of fullerene C<sub>60</sub> in liquid ammonia. *J. Am. Chem. Soc.* **1992**, *114*(27), 11004-11006.
- Schuster, D. I.; Nuber, B.; Vail, S. A.; MacMahon, S.; Lin, C.; Wilson, S. R.; Khong, A. Synthesis, photochemistry and photophysics of stilbene-derivatized fullerenes. *Photochem. Photobiol. Sci.* **2003**, *2*(3), 315-321.
- Guldi, D. M. Small reorganization energy of fullerenes in charge separation processes. *Spectrum* **2003**, *16*(1), 8-11, 23.
- Safonov, I. G.; Baran, P. S.; Schuster, D. I. Synthesis and photophysics of a novel porphyrin-C<sub>60</sub> hybrid. *Tetrahedron Lett.* (1997), *38*(47), 8133-8136.

12. Carbonera, D.; Di Valentin, M.; Corvaja, C.; Agostini, G.; Giacometti, G.; Liddell, P. A.; Kuciauskas, D.; Moore, A. L.; Moore, T. A.; Gust, D. EPR Investigation of Photoinduced Radical Pair Formation and Decay to a Triplet State in a Carotene-Porphyrin-Fullerene Triad. *J. Am. Chem. Soc.* **1998**, *120*(18), 4398-4405.
13. Zhou, Z.; Schuster, D. I.; Wilson, S. R. Selective Syntheses of Novel Polyether Fullerene Multiple Adducts. *J. Org. Chem.* **2003**, *68*(20), 7612-7617.
14. Guldi, D. M. Molecular porphyrin-fullerene architectures. *Pure App. Chem.* **2003**, *75*(8), 1069-1075.
15. Liddell, P. A.; Kodis, G.; Andreasson, J.; de la Garza, L.; Bandyopadhyay, S.; Mitchell, R. H.; Moore, T. A.; Moore, A. L.; Gust, D. Photonic Switching of Photoinduced Electron Transfer in a Dihydropyrene-Porphyrin-Fullerene Molecular Triad. *J. Am. Chem. Soc.* **2004**, *126*(15), 4803-4811.
16. Li, K.; Schuster, D. I.; Guldi, D. M.; Herranz, M. A.; Echegoyen, L. Convergent Synthesis and Photophysics of [60]Fullerene/Porphyrin-Based Rotaxanes. *J. Am. Chem. Soc.* **2004**, *126*(11), 3388-3389.
17. MacMahon, S.; Fong, R. II; Baran, P. S.; Safonov, I.; Wilson, S. R.; Schuster, D. I. Synthetic Approaches to a Variety of Covalently Linked Porphyrin-Fullerene Hybrids. *J. Org. Chem.* **2001**, *66*(16), 5449-5455.
18. Guldi, D. M.; Nuber, B.; Bracher, P. J.; Alabi, C. A.; MacMahon, S.; Kukol, J. W.; Wilson, S. R.; Schuster, D. I. Synthesis and Photophysics of a Copper-Porphyrin-Styrene-C<sub>60</sub> Hybrid. *J. Phys. Chem. A.* **2003**, *107*(18), 3215-3221.
19. Chiang L. Y.; Padmawar, P. A.; Canteenwala, T.; Tan, L-S.; He, G. S.; Kannan, R.; Vaia, R.; Lin, T-C.; Zheng, Q.; Prasad, P. N. Synthesis of C<sub>60</sub>-diphenylaminofluorene dyad with large 2PA cross-sections and efficient intramolecular two-photon energy transfer. *Chem. Commun.* **2002**, *17*, 1854-1855.
20. Luo, H.; Fujitsuka, M.; Araki, Y.; Ito, O.; Padmawar, P.; Chiang, L. Y. Inter- and Intramolecular Photoinduced Electron-Transfer Processes between C<sub>60</sub> and Diphenylaminofluorene in Solutions. *J. Phys. Chem. B.* **2003**, *107*(35), 9312-9318.
21. Kannan, R.; He, G. S.; Yuan, L.; Xu, F.; Prasad, P. N.; Dombroskie, A. G.; Reinhardt, B. A.; Baur, J. W.; Vaia, R. A.; Tan, L-S. Diphenylaminofluorene-Based Two-Photon-Absorbing Chromophores with Various  $\pi$ -Electron Acceptors. *Chem. Mater.* **2001**, *13*(5), 1896-1904.
22. Kannan, R.; He, G. S.; Lin, T-C.; Prasad, P. N.; Vaia, R. A.; Tan, L-S. Toward Highly Active Two-Photon Absorbing Liquids. Synthesis and Characterization of 1,3,5-Triazine-Based Octupolar Molecules. *Chem. Mater.* **2004**, *16*(1), 185-194.
23. He, G. S.; Lin, T-C.; Prasad, P. N.; Kannan, R.; Vaia, R. A.; Tan, L-S. Study of Two-Photon Absorption Spectral Property of a Novel Nonlinear Optical Chromophore Using Femtosecond Continuum. *J. Phys. Chem. B.* **2002**, *106*(43), 11081-11084.
24. Baur, J. W.; Alexander, M. D., Jr.; Banach, M.; Denny, L. R.; Reinhardt, B. A.; Vaia, R. A.; Fleitz, P. A.; Kirkpatrick, S. M. Molecular Environment Effects on Two-Photon-Absorbing Heterocyclic Chromophores. *Chem. Mater.* **1999**, *11*(10), 2899-2906.

25. Tang, C. W.; VanSlyke, S. A. Organic electroluminescent diodes. *App. Phys. Lett.* **1987**, *51*(12), 913-915.
26. Tang, C. W.; VanSlyke, S. A.; Chen, C. H. Electroluminescence of doped organic thin films. *J. App. Phys.* **1989**, *65*(9), 3610-16.
27. Chan, L.-H.; Lee, R.-H.; Hsieh, C.-F.; Yeh, H.-C.; Chen, C.-T. Optimization of High-Performance Blue Organic Light-Emitting Diodes Containing Tetraphenylsilane Molecular Glass Materials. *J. Am. Chem. Soc.* **2002**, *124*(22), 6469-6479.
28. Kastner, J.; Paloheimo, J.; Kuzmany, H. Fullerene field-effect transistors. *Springer Series in Solid-State Sciences*. **1993**, *113* (Electronic Properties of High-Tc Superconductors), 512-15.
29. Imahori, H.; Kashiwagi, Y.; Hasobe, T.; Kimura, M.; Hanada, T.; Nishimura, Y.; Yamazaki, I.; Araki, Y.; Ito, O.; Fukuzumi, S. Porphyrin and fullerene-based artificial photosynthetic materials for photovoltaics. *Thin Solid Films* **2004**, *451-452*, 580-588.
30. Yamada, H.; Imahori, H.; Nishimura, Y.; Yamazaki, I.; Ahn, T. K.; Kim, S. K.; Kim, D.; Fukuzumi, S. Photovoltaic Properties of Self-Assembled Monolayers of Porphyrins and Porphyrin-Fullerene Dyads on ITO and Gold Surfaces. *J. Am. Chem. Soc.* **2003**, *125*(30), 9129-9139.
31. Bingel, C. Cyclopropanation of fullerenes. *Chem. Ber.* **1993**, *126*(8), 1957-1959.